A mixed-ligand approach for a gigantic and hollow heterometallic cage $\{Ni_{64}Gd_{96}\}$ for gas separation and magnetic cooling applications

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With the support of the National Natural Science Foundation of China, the research team led by Prof. Zheng Yanzhan (郑彦臻) at the Frontier Institute of Science and Technology, Xi'an Jiaotong University, recently reported a gigantic rare-earth transition metal cuboidal hollow cluster $\{Ni_{64}Gd_{96}\}$ that exhibits high selectivity for absorbing CO_2 over CH_4 or N_2 at room temperature and large magnetocaloric effects at low temperatures, which was published in *Angew Chem Int Ed* (2016, 55: 9375-9379) and highlighted by *Molecular Magnetism Web*.

Heterometallic 3d-4f clusters possessing aesthetically beautiful architectures and potential applications have attracted increasing interest. Up to now, most of the 3d-4f clusters were constructed by a single multidentate ligand containing both N- and O-donor atoms. Prof. Zheng and his group instead used a mixed-ligand approach, which led to the isolation of the highest-nuclearity 3d-4f nanocage $\{Ni_{64}Gd_{96}\}$ (Figure). More interestingly, this giant cage is porous and possesses a pure inorganic cuboidal framework comprising 160 metal ions, which are unusually inter-linked by only hydroxy and carboxylate O atoms. The inner cavity of the cage is *ca.* 1.4 nm in diameter, while the external length of the cage is *ca.* 3.2 nm. Adjacent clusters are piled up into a 3D porous extended structure via extensive H-bonding interactions. Importantly, gas adsorption experiments show $\{Ni_{64}Gd_{96}\}$ can selectively absorb carbon dioxide over methane and nitrogen ($CO_2/CH_4 = 20$ and $CO_2/N_2 = 94$) at room temperature, which is even better than many metal-organic framework materials. Moreover, magnetic entropy changes $-\Delta S_M$ obtained from isothermal magnetization data at various temperatures give a large value of 42.8 $J \cdot kg^{-1} \cdot K^{-1}$ at 3 K and 7 Tesla, which is the largest among 3d-4f coordination clusters.

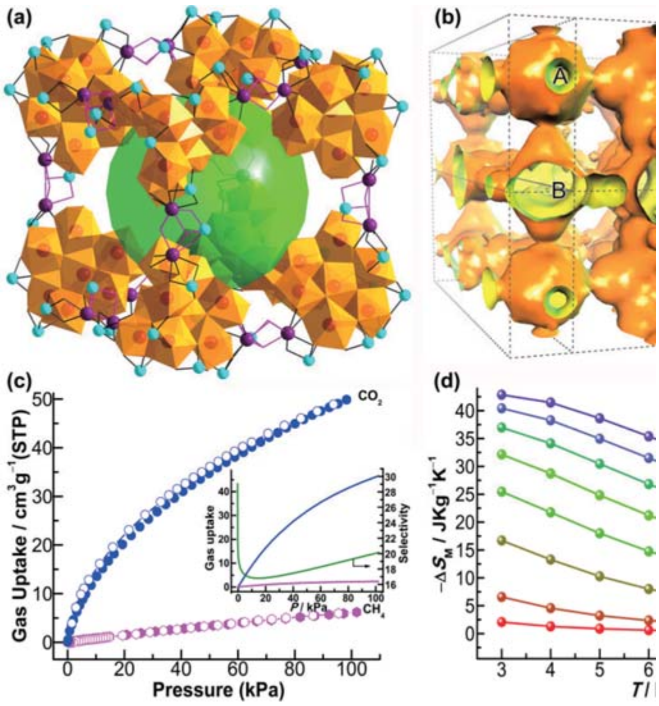

Figure (a) The polyhedron structure of $\{Ni_{64}Gd_{96}\}$ core; (b) the surface view for the 3D porous structure; (c) adsorption isotherms of CH_4, and CO_2 at 298 K for $\{Ni_{64}Gd_{96}\}$. Inset: IAST predicted selectivity for CO_2/CH_4 adsorption; (d) the plots of $-\Delta S_M$ vs T for $\{Ni_{64}Gd_{96}\}$.

Therefore, this result not only provided a new approach for synthesizing giant clusters but also discovered a new species of porous coordination cluster with pure inorganic framework and multi-functionality.